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(54) HYDROXY POLYAMIDE AND COMPOSITION THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a hydroxy polyamide, and to provide a positive-type photosensitive resin composition containing the hydroxy polyamide, exhibiting high photographic sensitivity, and satisfying such heat resistance and mechanical performance in a high level as required when the composition is used as a surface protection film for a semiconductor device and an interlayer insulation film therefor.

SOLUTION: This hydroxy polyamide is expressed by the general formula (R1 and R3 are each a tetravalent aromatic residue; R2 is a divalent aromatic residue; n is an integer of 2-500; and Z is a divalent organic residue). The positive-type photosensitive resin composition is obtained by using the composition.

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CLAIMS

[Claim(s)]

[Claim 1] A hydroxy polyamide shown by the following general formula.

[Formula 1]

$$Z = \begin{bmatrix} O & O & OH \\ O & O & OH \\ N-R_1 & H & OH \\ OH & H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-R_2-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-R_2-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-R_2-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-R_2-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-R_2-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-R_2-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-R_3-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-R_3-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-R_3-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-R_3-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-R_3-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-R_3-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-R_3-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} O & OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} OH \\ N-C-N-R_3 \\ H & OH \\ \end{bmatrix}_{n} = \begin{bmatrix} OH \\ N-C-N-R_3 \\$$

Even if the same the inside R1 and R3 of [, however a formula, the tetravalent aromatic series radical which may differ, and R2 are divalent aromatic series radicals. n is the integer of 2-500 and Z expresses a divalent organic radical.]

[Claim 2] (A) A hydroxy polyamide according to claim 1, the 100 weight sections and (B) photosensitivity quinone diazide compound, a positive type photopolymer constituent that uses 1 - 50 weight section as an indispensable component.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the photopolymer constituent using the hydroxy polyamide and this polymer of the alkali fusibility which is the precursor of a heat-resistant-resin material.

[0002]

[Description of the Prior Art] From the former, the polyimide resin having the outstanding thermal resistance, an electrical property, a mechanical characteristic, etc. is used for the surface-protection film of a semiconductor device, and the interlayer insulation film. Generally this polyimide resin is offered in the form of a photosensitive polyimide precursor constituent, can make it form easily by performing patterning according this to spreading and an activity beam of light, development, heat imide-ized processing, etc., and has the feature that large process compaction is attained compared with conventional non-light-sensitive polyimide.

[0003] However, it is necessary to use the organic solvent of large quantities, such as an N-methyl-2-pyrrolidone, as a developer, and the cure against a deorganic solvent has been demanded from the rise of an environmental problem in recent years etc. in the development process. in response, the proposal of the heat-resistant photopolymer material in which development is possible should recently various-kinds-make it be the same as that of a photoresist in a thin alkali aqueous solution -- *****. The method of mixing with optical active ingredients, such as quinone diazide, and using especially, the hydroxy polyamide, for example, the poly benzoxazole (PBO) precursor, of aquosity alkali fusibility, attracts attention in recent years. (Provisional-Publication-No. No. 96162 [63 to] official report etc.) [0004] It is exposure and the development by the alkali aqueous solution, formation of a positive type pattern is easy for these, and they are good, and since they have the heat-curing film property equivalent to polyimide, they attract attention as promising alternate material of an organic solvent development mold polyimide precursor. [of development nature and conservation stability] However, the PBO precursor obtained by the method indicated until now also still has many troubles.

deterioration of the diazo quinone compound used in a positive-resist constituent is promoted, and stability gets worse extremely. In order to improve this, the method of changing an amino terminal into another functional group through amide association is proposed (refer to JP,5-197153,A). Surely according to this method, the stability of the diazo quinone compound in a constituent is improved. However, the constituent obtained by doing in this way had the defect that sensitivity was low. In order to raise the throughput of a final product, improvement in sensitivity was called for, but the photopolymer constituent was not able to meet the demand, when the polymer mentioned above was used. Furthermore, the defect that it was difficult to obtain a low detailed pattern also had an adhesive property to the wafer of a paint film at the time of a development process.

[Problem(s) to be Solved by the Invention] In the positive-resist constituent containing a diazo quinone

compound, formation of a positive type pattern is possible for this invention, it shows high sensitivity according to the development process by exposure and the alkali aqueous solution, and is to offer further the thermal resistance demanded as the surface-protection film of a semiconductor device, and an interlayer insulation film use, the hydroxy polyamide which is the heat-resistant-resin precursor which is satisfied with a high level of the dynamics engine performance, and the photopolymer constituent using this polymer.

[0007]

[Means for Solving the Problem] this invention persons perceived an end group of polymer, and they inquired wholeheartedly in order to have not produced deterioration of a diazo quinone compound in the above-mentioned positive-resist constituent and to have made outstanding thermal resistance and an outstanding hardening film property discover. Consequently, it came to complete a header and this invention for said property being satisfied and it being compatible in exposure section dissolution clearance nature and unexposed section dissolution resistance with high level also in the time of development using 2.38% tetramethylammonium hydroxide (TMAH) aqueous solution for the first time by changing a polymer end amino group into an imide radical.

[0008] That is, this invention offers a hydroxy polyamide shown by the following general formula. [0009]

[Formula 2]

[0010] Even if the same the inside R1 and R3 of [, however a formula, the tetravalent aromatic series radical which may differ, and R2 are divalent aromatic series radicals. n is the integer of 2-150 and Z expresses a divalent organic radical.] Moreover, this invention also offers the hydroxy polyamide of (A) above, the 100 weight sections and (B) photosensitivity quinone diazide compound, and the positive type photopolymer constituent that uses 1 - 50 weight section as an indispensable component. [0011] Hereafter, this invention is explained to details. In order to obtain the hydroxy polyamide of this invention, the polycondensation of aromatic series dicarboxylic acid or its derivative, and screw - (Oaminophenol) is carried out first. As the dicarboxylic acid containing the divalent aromatic series radical R2 used for this invention, or its derivative Phthalic-acid, isophthalic acid, terephthalic-acid, 4, and 4'diphenyl ether dicarboxylic acid, - diphenyl ether dicarboxylic acid, and 4 '3, 3'-diphenyl ether dicarboxylic acid, [3, and] - biphenyl dicarboxylic acid, and 4 and 4'3, 4'-biphenyl dicarboxylic acid, biphenyl dicarboxylic acid, and 3 and 3 '4, 4'-benzophenone dicarboxylic acid, - benzophenone dicarboxylic acid, and 4 '3, 3'-benzophenone dicarboxylic acid, [3, and] - diphenylsulfone dicarboxylic acid, and 4 and 4 '3, 4'-diphenylsulfone dicarboxylic acid, - diphenylsulfone dicarboxylic acid, and 3 and 3 '4, 4'-hexafluoro isopropylidene 2 benzoic acid, A 4 and 4'-dicarboxy diphenyl amide, 1, 4-FENI range ethanoic acid, 1 and 1-screw (4-carboxyphenyl)-1-phenyl - 2, 2, and 2-trifluoro ethane, Screw (4carboxyphenyl) tetra-phenyl disiloxane, screw (4-carboxyphenyl) tetramethyl disiloxane, A screw (4carboxyphenyl) sulfone, screw (4-carboxyphenyl) methane, 5-t-butyl isophthalic acid, 5-BUROMO isophthalic acid, 5-fluoro isophthalic acid, A 5-chloro isophthalic acid, 2, and 2-screw-(pcarboxyphenyl) propane, Although an activity ester object with 4 and 4' -(p-phenylene dioxy) 2 benzoic acid, 2, 6-naphthalene dicarboxylic acid or these acid chloride objects, hydroxy benzotriazol, etc. can be mentioned, it is not limited to these, moreover, these things are independent -- or you may mix and use. [0012] moreover, as screw - (O-aminophenol) containing the tetravalent aromatic series radicals R1 and R3 suitably used by this invention For example, 3, a 3'-dihydroxy benzidine, 3, the 3'-diamino -4, a 4'dihydroxy biphenyl, 4, the 4'-diamino -3, a 3'-dihydroxy biphenyl, 3, 3'-diamino -4, 4'-dihydroxy diphenylsulfone, 4 4'-diamino -3, 3'-dihydroxy diphenylsulfone, A screw-(3-amino-4-hydroxyphenyl)

methane, 2, and 2-screw-(3-amino-4-hydroxyphenyl) propane, 2 and 2-screw-(3-amino-4-hydroxyphenyl) hexafluoropropane, 2 and 2-screw-(4-amino-3-hydroxyphenyl) hexafluoropropane, A screw-(4-amino-3-hydroxyphenyl) methane, 2, and 2-screw-(4-amino-3-hydroxyphenyl) propane, 4 4'-diamino -3, a 3'-dihydroxy benzophenone, 3, the 3'-diamino -4, a 4'-dihydroxy benzophenone, 4 4'-diamino -3, 3'-dihydroxy diphenyl ether, 3, 3'-diamino Although -4, 4'-dihydroxy diphenyl ether, 1, the 4-diamino -2, 5-dihydroxybenzene, etc. are mentioned, it is not limited to these moreover, these things are independent -- or you may mix and use.

[0013] In the case of the activity ester object of aromatic series dicarboxylic acid chloride or aromatic series dicarboxylic acid, the hydroxy polyamide of this invention can be obtained by mixing with screw - (O-aminophenol) under basic compound existence, such as a suitable pyridine in a solvent, although it is the polycondensation object which consists of the above-mentioned raw material. However, when using aromatic series dicarboxylic acid, a suitable condensing agent is needed. As such a condensing agent, a well-known dehydration condensing agent can use conventionally, for example, dicyclohexylcarbodiimide, 1-ethoxycarbonyl-2-ethoxy -1, 2-dihydroquinoline, 1, and 1'-carbonyl dioxy-G 1 and 2, 3-benzotriazol, N,N'-disuccinimidylcarbonate, phosphite, etc. can be mentioned. Among these, in the case of dicyclohexylcarbodiimide, it is 1-hydroxy. - Using with 1, 2, and 3-benzotriazol is desirable.

[0014] After preparing so that the both ends of polymer may serve as an amino group by these methods, the end amino group is made to condense with an acid anhydride. As an example of the acid anhydride used here, 1, 2-cyclohexane dicarboxylic acid anhydride, The 4-methylcyclohexane -1, 2-dicarboxylic acid anhydride, the 3-methylcyclohexane -1, 2-dicarboxylic acid anhydride, The 4-cyclohexene -1, 2dicarboxylic acid anhydride, 1, 2-cyclopentane dicarboxylic acid anhydride, 1, 2-cyclobutane dicarboxylic acid anhydride, 1, 2-cyclopropane dicarboxylic acid anhydride, 5-norbornene -2, 3dicarboxylic acid anhydride, norbornane -2, 3-dicarboxylic acid anhydride, A 2, 3-pyridine dicarboxylic acid anhydride, 1, and 1-cyclopentane 2 acetic-acid anhydride, an anhydrous citraconic acid, anhydrous diphenic acid, and anhydrous -- 3, 6-epoxy -1, 2 and 3, and 6-tetrahydrophtal acid -- an anhydrous glutaric acid, itaconic acid anhydride, a maleic anhydride, phthalic anhydride, anhydrous 4-ethynyl phthalic acid, an anhydrous amber acid, and anhydrous -- 1, 2-naphthalic acid, and anhydrous -although 1, 8-naphthalic acid, anhydrous oleic acid, etc. are mentioned, it is not limited to these. [0015] The hydroxy polyamide of this invention can be obtained by making the end of the end amino group of polymer, and the condensate of an acid anhydride obtained at the above-mentioned reaction imide-ize. As the method of imide-izing, various well-known methods, such as heating, a dehydrating agent, a dehydrating agent, a basic catalyst, and a basic catalyst, can be used. As a dehydrating agent used at this time, a well-known dehydrating agent can be used conventionally. For example, an acetic anhydride, a propionic anhydride, a benzoic anhydride, anhydrous trifluoroacetic acid, Acetyl chloride, tosyl chloride, mesyl chloride, KURORUGI acid ethyl, Triphenyl phosphine, dibenzo imidazolyl disulfide, dicyclohexylcarbodiimide, N and N'-carbonyldiimidazole, 2-ethoxy-1-ethoxycarbonyl -1, a 2dihydroquinoline, When using a basic catalyst, oxalic acid N and N'-ЛSUKUSHINIMIЛRU ester etc. A pyridine, Picoline, 2, 6-lutidine, a collidine, triethylamine, N-methyl morpholine, Although 4-N and N' diazabicyclo [- dimethylamino pyridine, isoquinoline, triethylamine, 1, and 4-] [2.2.2] octane, 1, and 8diazabicyclo [5.4.0]-7-undecene etc. is mentioned, it is not limited to these.

[0016] Furthermore, if an imide-ized method is chosen, when both ends add simultaneously the acid anhydride and imide-ized agent for end condensation to the polymer of the amino group, the hydroxy polyamide of this invention can be obtained, without going via intermediate field. Moreover, as an option which obtains the hydroxyl polyamide of this invention, after making only one amino group of screw - (O-aminophenol) react with an acid anhydride, the compound made to imide-ize is compounded and this may be added at the time of the polycondensation of aromatic series dicarboxylic acid or its derivative, and screw - (O-aminophenol).

[0017] Generally the polar solvent which dissolves the hydroxy polyamide to generate thoroughly as an organic solvent used for the above-mentioned reaction is desirable, for example, a N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N.N-dimethylformamide, dimethyl sulfoxide, tetramethylurea,

gamma-butyrolactone, etc. are mentioned. In addition to this polar solvent, as the ketones which are a common organic solvent, ester, lactone, ether, halogenated hydrocarbon, and hydrocarbons in addition, for example An acetone, a methyl ethyl ketone, methyl isobutyl ketone, a cyclohexanone, Methyl acetate, ethyl acetate, butyl acetate, oxalic acid diethyl, ethylene glycol wood ether, Diethylene-glycol wood ether, a tetrahydrofuran, dichloromethane, 1,2-dichloroethane, 1, 4-dichlorobutane, a chlorobenzene, o-dichlorobenzene, a hexane, a heptane, benzene, toluene, a xylene, etc. can be used. Although a resist constituent can be presented as it is, this resultant can be thrown in in the poor solvent of hydroxy polyamides, such as water or a methanol, if needed, and can also be refined and used by repeating reprecipitation further.

[0018] The hydroxy polyamide by this invention is useful in order to manufacture the positive-resist constituent which uses a photoresist constituent, especially a photosensitive diazo quinone compound as a sensitization agent as mentioned above. Such a photosensitive diazo quinone compound is a compound which has 1 and 2-benzoquinone diazido or 1, and 2-naphthoquinonediazide structure, and is the well-known matter by U.S. Pat. No. 2,772,972, 2,797,213, 3,669,658, etc. As a concrete example of such a compound, the following are mentioned, for example.

[0019] [Formula 3]

[0020] [Formula 4] 式中Qは、水業原子、

から選ばれ、各化合物においてそれぞれ少なくとも1個は

である。

[0021] In addition, to a positive-resist constituent, additives, such as a phenolic compound, a leveling agent, and a silane coupling agent, can be added if needed. With the above-mentioned sensitization agent and an additive, it dissolves in a solvent and is used by making the hydroxy polyamide of this invention into the shape of a varnish. As the solvent in this case, a N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N.N-dimethylformamide, gamma-butyrolactone, dimethyl sulfoxide, Diethylene-glycol wood ether, diethylene-glycol diethylether, Diethylene-glycol dibutyl ether, propylene glycol monomethyl ether, Dipropylene glycol monomethyl ether, propylene-glycol-monomethyl-ether acetate, Methyl lactate, ethyl lactate, butyl lactate, methyl -1, 3-butylene-glycol acetate, 1, the 3-butylene-glycol-3-monomethyl ether, methyl pyruvate, pyruvic-acid ethyl, methyl-3-methoxy propionate, etc. are mentioned, and it may be independent, or you may mix and use.

[0022] The operation of the positive-resist constituent used in this invention applies this constituent to a semiconductor wafer first. Revolution spreading using a spinner as the method of application, fuel-spray spreading using a spray coater, immersion, printing, roll coating, etc. are mentioned, among these thickness can be easily controlled by changing the rotational frequency of a spinner, when it is the revolution applying method, and the thickness after the last hardening is made to be set to 0.1-20 micrometers.

[0023] Next, it prebakes at 80-140 degrees C, and chemical rays are irradiated after drying a paint film at a desired pattern configuration. As chemical rays, although an X-ray, an electron ray, ultraviolet rays, a visible ray, etc. can be used, a thing with a wavelength of 200-500nm is desirable. Next, a relief pattern is obtained by carrying out dissolution clearance of the exposure section with a developer. [0024] As a developer used, a sodium hydroxide, a potassium hydroxide, a sodium carbonate, Inorganic alkali, such as a sodium silicate, a meta-sodium silicate, and aqueous ammonia Primary amine, such as ethylamine and n propylamine, diethylamine, The 3rd amines, such as the 2nd amines, such as G n propylamine, triethylamine, and methyl diethylamine, Alcoholic amines, such as dimethylethanolamine and triethanolamine, The aqueous solution which carried out suitable amount addition of alcohols and surfactants, such as a methanol and ethanol, can be suitably used for the aqueous solution of alkali, such as quarternary ammonium salt, such as tetramethylammonium hydroxide and tetraethylammonium hydroxide, and this. As the development method, methods, such as a spray, a paddle, immersion, and an ultrasonic wave, are possible.

[0025] Next, although the rinse of the relief pattern formed by development is carried out, distilled water is used as a rinse. Next, by heat-treating at 300-400 degrees C, the pattern excellent in the thermal resistance which has an oxazole ring can be obtained.

[0026]

[Embodiment of the Invention] Based on an example, the example of the concrete operation gestalt of

this invention is explained below.

[0027]

[Example 1] In separable hula SURASUKO of capacity 1L, mixed stirring of the 231g [of N,N-dimethylacetamide] (DMAc), pyridinesg [7.91] (0.1 mols) and 2, and 2-screw (3-amino-4-hydroxyphenyl)-hexafluoropropane 65.93g (0.18 mols) was carried out at the room temperature (25 degrees C), and diamine was dissolved. this -- separately -- diethylene-glycol wood ether (DMDG) 133g -- that in which 4 and 4'-diphenyl ether dicarboxylic acid dichloride 44.27g (0.15 mols) was dissolved was dropped from the dropping funnel at inside. Under the present circumstances, the separable flask was cooled by the 15-20-degree C water bath. The time amount which dropping took was 40 minutes, and the reaction liquid temperature was 30 degrees C at the maximum.

[0028] From dropping termination, to reaction mixture after 60-minute stirring neglect 5-norbornene -2, 29.55g (0.18 mols) of 3-dicarboxylic acid anhydrides, After adding pyridine 34.80g (0.44 mols) and agitating at 20-25 degrees C for 27 hours, After cooling at 0 degree C by the ice bath, into DMDG12.38g, what dissolved dicyclohexylcarbodiimide (DCC) 12.38g (0.06 mols) was added, reaction mixture was returned at the room temperature, it agitated for 3 hours, and 100% of all the amine end groups of a polymer chain were closed by the imide radical.

[0029] Then, after filtering the above-mentioned reaction mixture and removing insoluble matter, it was dropped at the water of 2L under high-speed stirring, and the distributed deposit of the polymer was carried out, these was collected, the vacuum drying was suitably performed after rinsing and dehydration, and the hydroxy polyamide (NI-1) of the GPC weight average molecular weight 9600 (polystyrene conversion) was obtained. Furthermore, when purification of polymer is required, it is possible to carry out by the following methods. That is, it processed by pouring the polymer solution which remelted the polymer obtained above to DMDG400g with ion exchange water to the glass column with which the cation exchange resin and anion exchange resin 49g and 41g which were replaced by DMDG after washing were filled up, respectively. Thus, the refined polymer solution was dropped at ion-exchange-water 5L, and after separating and washing the polymer which deposits in that case, the polymer refined by performing a vacuum drying was able to be obtained.

[0030] When the characteristic absorption of the imide radical of 1384 and 1772cm-1 appeared with IR chart, it checked that the end of the obtained polymer was an imide radical.

[Example 2] In separable hula SURASUKO of capacity 1L, mixed stirring of the tetrahydrofuran (THF) 396g, pyridinesg [9.49] (0.12 mols) and 2, and 2-screw (3-amino-4-hydroxyphenyl)-hexafluoropropane 131.85g (0.36 mols) was carried out at the room temperature (25 degrees C), and diamine was dissolved. That in which 5-norbornene -2 and 19.70g (0.12 mols) of 3-dicarboxylic acid anhydrides were dissolved was separately dropped from the dropping funnel into THF59.1g at this. The time amount which dropping took was 80 minutes, and the reaction liquid temperature was 26 degrees C at the maximum. [0032] The through pyridine was removed for the glass column with which reaction mixture was filled up into cation-exchange-resin:Amberlyst 15 (ORGANO CORP. make) 30g from dropping termination after 6-hour stirring neglect. Next, after carrying out reduced pressure distilling off of the THF from this solution, the compound of the following structure and the mixture of 1:2 of 2 and 2-screw (3-amino-4-hydroxyphenyl)-hexafluoropropane were obtained at 95% of yield by carrying out a vacuum drying. When the characteristic absorption of the imide radical of that there is no absorption which shows the amide group of the 1650 or 1550cm-1 neighborhood with IR chart, 1384, and 1770cm-1 appeared, it checked that NMD had imide-ized.

[0033]

[Formula 5]

[0034] Next, in separable hula SURASUKO of capacity 1L, mixed stirring of the 74.76g [of this mixture], 231g [of N,N-dimethylacetamide] (DMAc), and pyridine 7.91g (0.1 mols) was carried out at the room temperature (25 degrees C), and it considered as the homogeneity solution. this -- separately -- diethylene-glycol wood ether (DMDG) 133g -- that in which 4 and 4'-diphenyl ether dicarboxylic acid dichloride 44.27g (0.15 mols) was dissolved was dropped from the dropping funnel at inside. Under the present circumstances, the separable flask was cooled by the 15-20-degree C water bath. The time amount which dropping took was 40 minutes, and the reaction liquid temperature was 30 degrees C at the maximum.

[0035] 3 hours after dropping termination The above-mentioned reaction mixture was dropped at the water of 2L under high-speed stirring, the distributed deposit of the polymer was carried out, these was collected, the vacuum drying was suitably performed after rinsing and dehydration, and the hydroxy polyamide (NI-2) of the GPC weight average molecular weight 9000 (polystyrene conversion) was obtained. Furthermore, when purification of polymer is required, it is possible to carry out by the following methods. That is, it processed by pouring the polymer solution which remelted the polymer obtained above to DMDG400g with ion exchange water to the glass column with which the cation exchange resin and anion exchange resin 49g and 41g which were replaced by DMDG after washing were filled up, respectively. Thus, the refined polymer solution was dropped at ion-exchange-water 5L, and after separating and washing the polymer which deposits in that case, the polymer refined by performing a vacuum drying was able to be obtained.

[0036] When the characteristic absorption of the imide radical of 1385 and 1772cm-1 appeared with IR chart, it checked that the end of the obtained polymer was an imide radical.

[The example 1 of a comparison] Except having not added DCC to the reaction mixture after polycondensation reaction termination, the same actuation as an example 1 was performed, and the hydroxy polyamide (NB) of the GPC weight average molecular weight 10000 (polystyrene conversion) by which the chain end was closed through the amide group was prepared. [0038]

[The example 2 of a comparison] Benzoyl chloride was used for the reaction mixture after polycondensation reaction termination instead of 5-norbornene -2 and 3-dicarboxylic acid anhydride, except having not added DCC to the reaction mixture after polycondensation reaction termination, the same actuation as an example 1 was performed, and the hydroxy polyamide (BZ) of the GPC weight average molecular weight 10800 (polystyrene conversion) by which the chain end was closed through the amide group was prepared.

[0039] (Assessment) Using the polymer obtained in each above-mentioned example and the example of a comparison, the positive-resist constituent was prepared, respectively and the varnish viscosity stability, a patterning property, the machine physical properties of an after [heat hardening] film, etc. were evaluated. First, after dissolving each polymer 100 weight section and the sensitization agent (** 6 reference) 15 weight section in the GBL160 weight section, it filtered with the 0.2-micrometer filter and the photopolymer constituent was prepared.

[Formula 6]

[0040]

$$QO \longrightarrow OQ$$
 $Q= O= S=O$
 $O= S=O$

[0041] (1) In the film machine physical-properties assessment above-mentioned photosensitivity constituent, the machine physical properties of the film obtained after heat hardening were evaluated. That is, homogeneity spreading of each varnish was carried out on the silicon wafer using the spin coater, and the sample was created so that Ushiro's thickness prebaked for 240 seconds on 100-degree-C hot plate might be set to about 12 micrometers. Next, this sample was set to the vertical mold cure furnace (made in Mitsuaki Lindbergh), curing (heat hardening processing) of 1 hour was performed at 320 degrees C among nitrogen-gas-atmosphere mind, and it considered as the poly benzoxazole (PBO) film which is a heat-resistant coat.

[0042] It exfoliated from the silicon wafer and machine physical-properties assessment was presented with this cure film. The assessment method is ASTM. It was based on D-882-88. A result is shown in a table 1. polymer NI- which reformed the polymer end group by the imide radical from this result -- it turned out that the constituent obtained from 1 and 2 shows the outstanding mechanical characteristic (especially ductility). As for NB which reformed the polymer end by the amide group, and the constituent obtained from BZ, in 320-degree-C cure, only the film inadequate [ductility] and brittle was obtained to it.

[0043]

[A table 1]

	ポリマー	キュア後 膜厚 (μm)	最大点 応力 (MPa)	ヤング率 (GPa)	破断点伸度 (%)
実施例1	NI-1	10.0	114.6	2.8	31.4
実施例 2	NI-2	9. 7	112.5	2.8	33.1
比較例1	NB	9. 9	110.3	2. 9	18.5
比較例2	BZ	9. 7	101.4	2. 6	4.3

[0044] (2) The paint film was formed so that it might become 10-micrometer thickness after prebaking in the way same on Si wafer processed in 250 degrees C and 15 minutes using the methanol solution of aminopropyl triethoxysilane 0.5% about the patterning assessment above-mentioned three kinds of photosensitive constituents as the sample creation for machine physical-properties assessment. Next, this was exposed by changing light exposure gradually by i-line stepper (NIKON make) through reticle with a test pattern. This exposure film was developed using the Clariant Japan AZ300MIF developer [a tetramethylammonium hydroxide (TMAH) 2.38% aqueous solution], negatives were developed by having adjusted developing time and the positive type pattern was formed so that the thickness after development might be set to 8 micrometers under conditions of 23 degrees. A result is shown in a table

[0045] The constituent using the polymer of the example of this invention showed the sensitivity, the resolution, and the adhesive property which were excellent under 2.38%TMAH aqueous solution development.

[0046] [A table 2]

	ポリマー	現像時間 (sec)	感度 (mJ/cm2)	解像度 (µm)	接着性
実施例1	N I - 1	180	350	4	良好
実施例2	NI-2	190	350	4	良好
比較例1	NB	150	450	5	剥がれあり
比較例2	ВZ	300	700	10	良好

[0047] From the above result, the photosensitive constituent using the hydroxy polyamide of this invention becomes what was extremely rich in flexibility also in [have the outstanding patterning property and] machine physical properties, and is sufficiently practical as the surface-protection film of a semiconductor device, and an interlayer insulation film use.

[0048]

[Effect of the Invention] As stated above, the hydroxy polyamide of this invention offers conventionally the surface-protection film of a semiconductor device, and the material which may be satisfied with high level of the dynamics engine performance demanded as an interlayer insulation film use by the well-known thing while attaining the outstanding alkali dissolution property under 2.38%TMAH aqueous solution development for which the response was difficult, and a patterning property.

[Translation done.]